(12) UK Patent Application (19) GB (11) 2 315 743 (13) A

(43) Date of A Publication 11.02.1998

(21) Application No 9616037.9

(22) Date of Filing 31.07.1996

(71) Applicant(s)
ECC International Limited

(Incorporated in the United Kingdom)

1015 Arlington Business Park, Theale, READING, RG7 4SA, United Kingdom

(72) Inventor(s)
Jonathan Stuart Phipps

(74) Agent and/or Address for Service
Derek J McCormack
ECC International Limited, Patent Dept, John Keay House, St.Austell, Cornwall, PL25 4DJ, United Kingdom

(51) INT CL^6
C02F 11/00 1/58 9/00

(52) UK CL (Edition P)
C1C CACF CJB CRCF C253 C332 C444 C461

(56) Documents Cited
None

(58) Field of Search
UK CL (Edition O) **C1C CACD CACF CJB CKB CM CRAL CRCF**
INT CL^6 **C02F 1/52 1/58 9/00 11/00 11/14**
Online: WPI, Claims, Japio, CAS

(54) Treating paper plant effluent

(57) Solid containing material derived from effluent or sludge from a plant for deinking paper, and containing calcium in the form of one or more insoluble calcium compounds is treated by causing dissolution of the calcium thereby forming a calcium ion-containing solution in which insoluble solids are suspended then separating the solution from the insoluble solids and adding to the solution one or more reagents to form a calcium salt precipitate.

GB 2 315 743 A

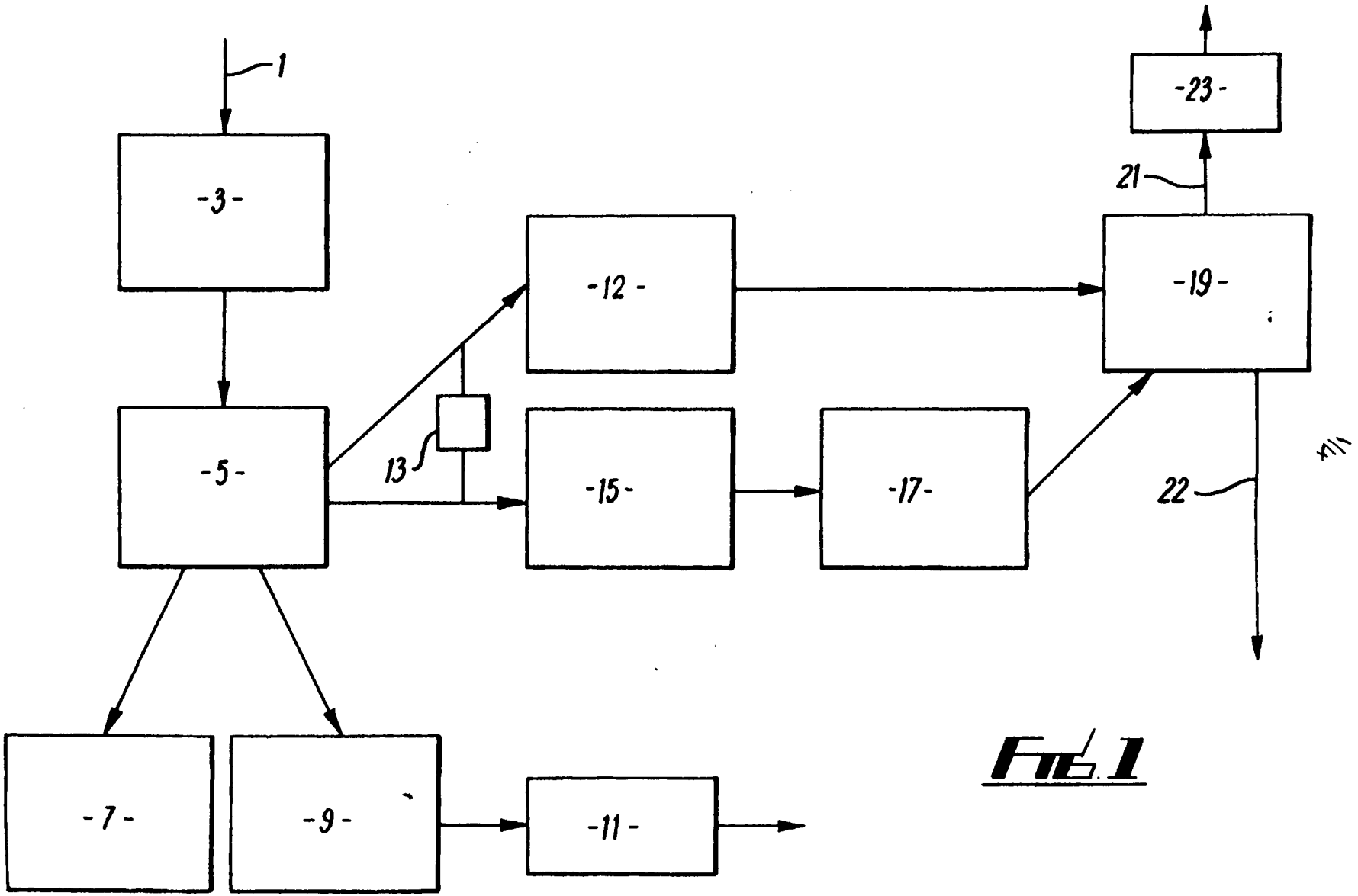

FIG. 1

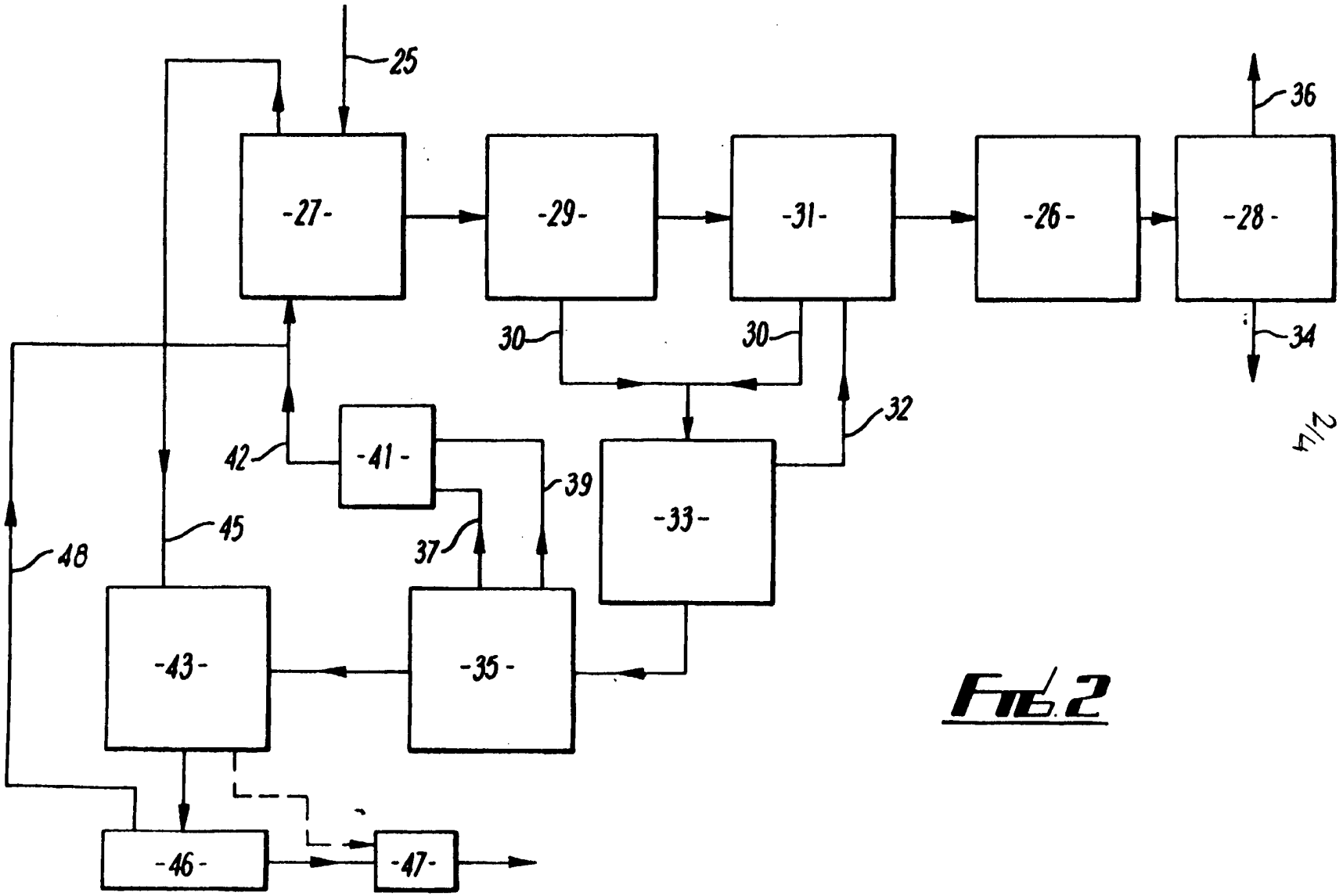

FIG. 2

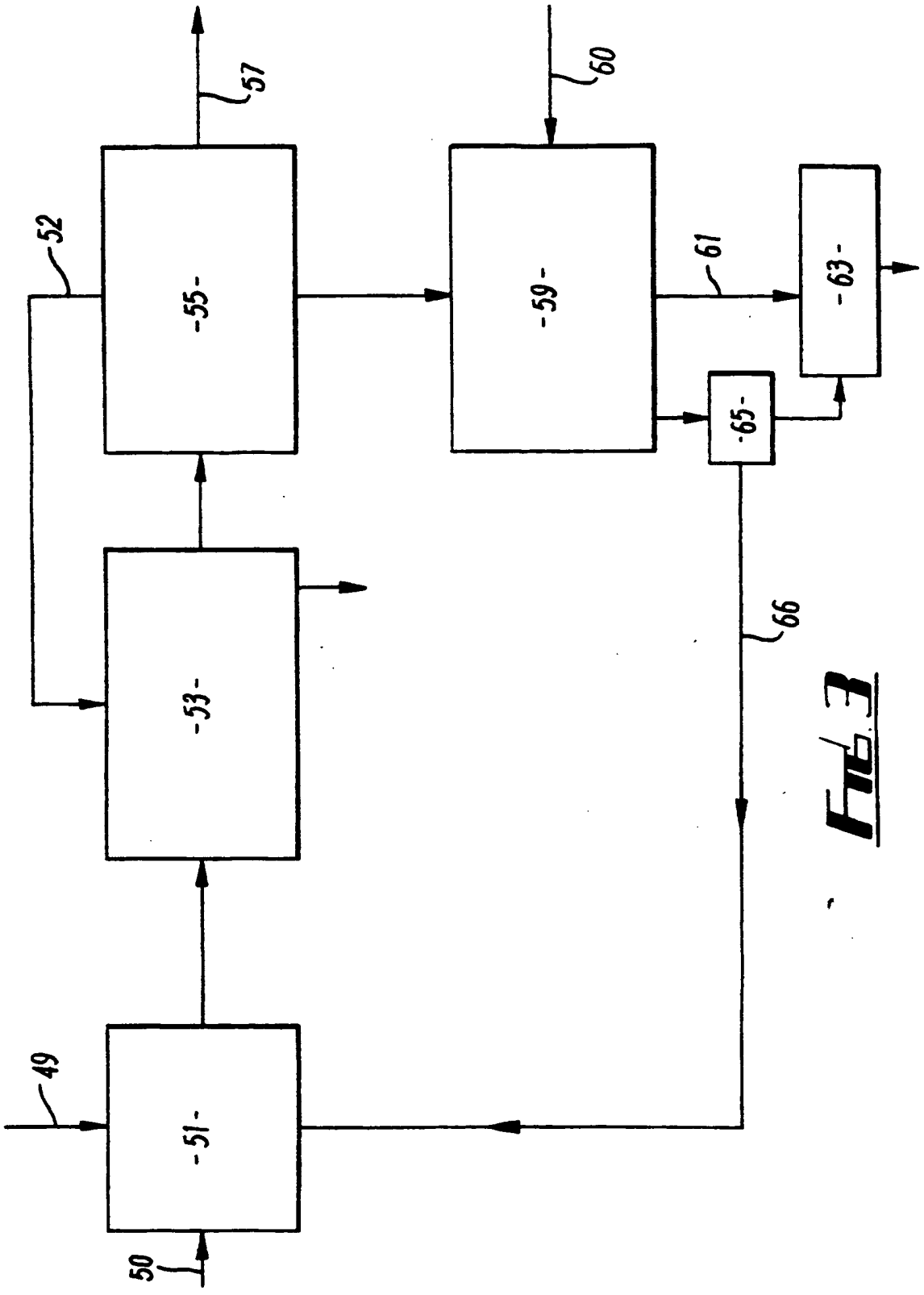

FIG 3

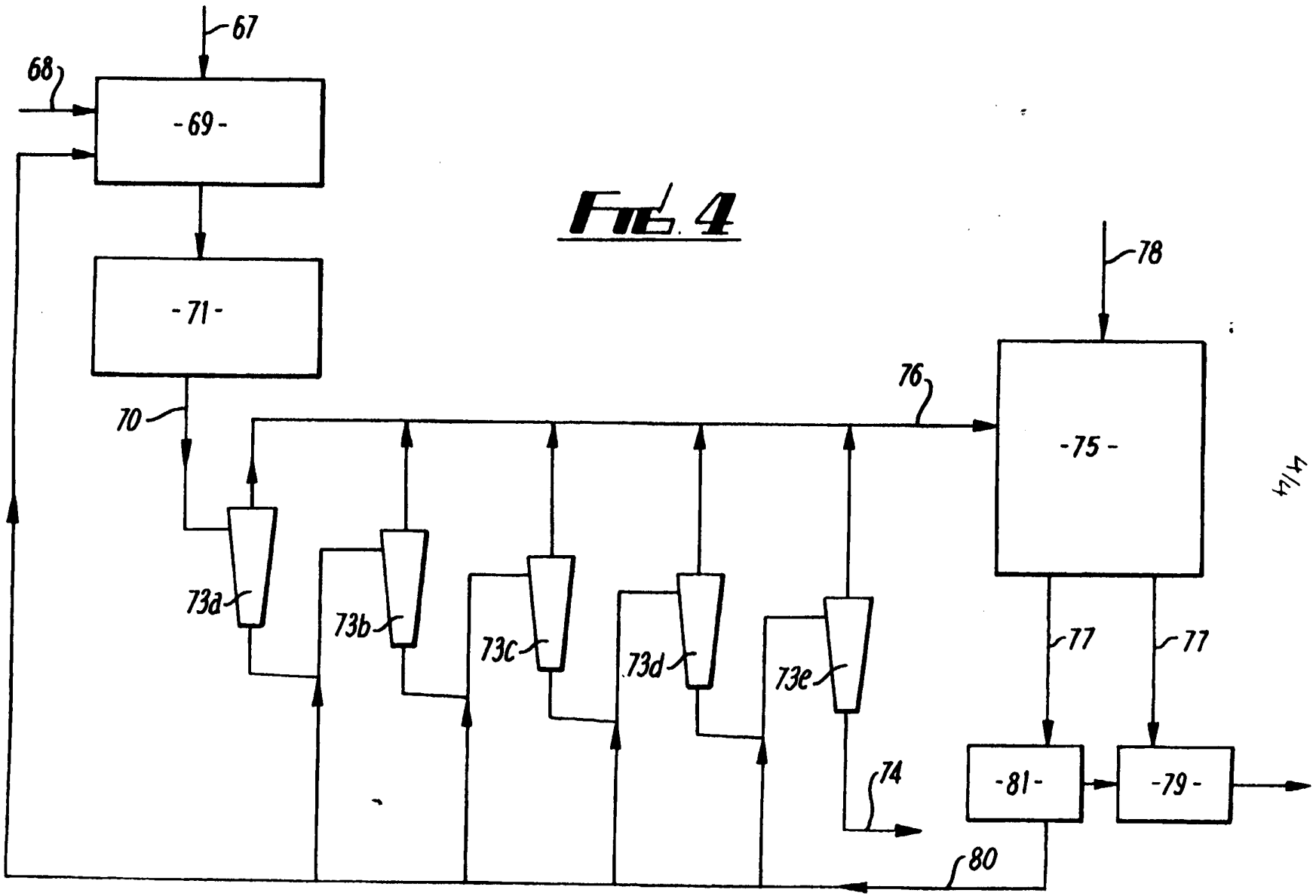

FIG. 4

2315743

TREATMENT OF SOLID CONTAINING MATERIAL DERIVED FROM EFFLUENT

The present invention relates to the treatment of solid containing material derived from effluent, especially to recover useful materials therefrom.

In particular, this invention is concerned with a method for recovering useful materials from what has hitherto been regarded as the waste material produced by an industrial plant for treating paper, especially for de-inking waste paper.

Paper and paperboard products are generally made by preparing a dilute aqueous suspension containing cellulosic fibres derived from wood or from some other suitable fibrous material, and de-watering the suspension on a moving wire mesh belt to form a sheet material. The suspension may also contain a proportion of a mineral filler material which improves the brightness and opacity of the finished paper or board. Natural cellulosic fibrous materials are generally expensive, and the trees or other plants from which they are obtained must be replaced if the balance of the environment is not to be disturbed. It is therefore desirable to incorporate in the aqueous suspension from which the sheet material is made a substantial proportion of cellulosic fibrous material which has been recovered from waste paper. Most waste paper which is recycled has been printed on at least one of its surfaces, and it is necessary to separate the printing ink residue from the cellulosic fibres if the recovered material is to be suitable for use as a starting material in a paper making process. If the ink is not separated, the fibrous material will generally be unacceptably dark in colour. Generally, printing ink contains elemental carbon (carbon black) and other dark material which causes the dark colouration.

Commercially operated processes for de-inking waste paper generally comprise a pulping stage in which the waste paper is subjected to mechanical agitation in water which also contains

sodium hydroxide which causes the fibres to swell, and which breaks down most ink vehicles by saponification or hydrolysis, sodium silicate which acts as a pH buffer and agglomerates detached ink particles to a convenient size, and a surfactant which wets the ink particles and helps to keep them in suspension. The suspension formed in the pulper is passed through a primary screening system in which heavy foreign bodies, such as staples, paper clips and pieces of grit are removed. The suspension passing through the screens is then fed to a treatment plant comprising one or more froth flotation cells, or one or more washing units, or a combination of washing units and flotation cells. The froth flotation cells are each provided near the bottom with a rotating impeller and means for admitting air under pressure in the form of fine bubbles in the region of the impeller. It may also be advantageous to add to the suspension, before it enters the flotation cell, a reagent known as a collector which attaches itself preferentially to the ink particles and increases their affinity with air relative to that with water. As a result, the ink particles are preferentially lifted by the air bubbles to the surface of the suspension in the flotation cell, where they are discharged in a froth product.

In the washing units the pulp is subjected to agitation in fresh or recycled water, optionally containing a dispersing agent, and the washed pulp is then drained on a screen of aperture size such as to retain the relatively long cellulosic fibres, while allowing to pass the mineral and organic particles and the fine fibre fragments.

The suspension which is discharged from the bottom of the flotation cell, and/or the suspension which passes the screens of the washing steps, is de-watered and the de-watered material, which consists of substantially de-inked cellulosic fibre material, may be subjected to further purification steps before being finally de-watered and dried for re-use in a sheet forming process.

The de-inking treatment plant reject consists of an aqueous effluent or sludge which is produced in large volumes.

The reject from some plants is discarded and transferred to a waste disposal site, eg. a landfill site. The reject from other plants is incinerated and this beneficially reduces the volume of the reject and generates useful heat energy from the combustion of organic components. The ash from the incineration is subsequently disposed of. However, in both cases, there is an undesirable cost and environmental impact associated with disposal. Also, potentially useful materials are wasted by the disposal process. The de-inking treatment plant reject generally contains, in addition to the ink particles, a substantial proportion of the inorganic filler particles which were originally present in the waste paper. These filler particles usually consist predominantly of a mixture of kaolin clay and calcium carbonate in various proportions, although other inorganic filler particles such as silicates, talc, calcium sulphate or titanium dioxide may also be present in minor proportions.

According to the present invention there is provided a method of treating solid containing material derived from effluent or sludge from a plant for de-inking paper, the material containing calcium in the form of one or more insoluble calcium compounds, the method including the steps of treating the material to cause dissolution of the calcium thereby forming a calcium ion-containing solution in which insoluble solids are suspended, separating the solution from the insoluble solids and adding to the solution one or more reagents to form a calcium salt precipitate.

The treated solid containing material may comprise the said effluent or sludge, optionally after diluting with water, and may comprise the particulate materials described hereinbefore. The said calcium compound may comprise calcium carbonate and/or sulphate.

Alternatively, the treated solid material may comprise ash obtained by incinerating the solid content of the de-inking effluent or sludge.

Where the treated material comprises de-inking plant effluent or sludge optionally diluted the said treatment to cause dissolution of the calcium may comprise addition of a dilute acid to provide the dissolution. The dilute acid used may comprise any one or more of the dilute acids known to form soluble calcium salts. Mineral acids such as hydrochloric acid are preferred.

Where the treated material comprises ash obtained from incinerating de-inking plant effluent or sludge, the ash will generally comprise a mixture of inorganic particulate material which will generally include calcium oxide. The particulate material may have undergone some degree of fusing together. It may be advantageous to apply a comminution step to the material prior to dissolution of the calcium. The comminution step may for example comprise grinding an aqueous suspension of the material to release the calcium oxide contained in the fused material. A chemical agent, eg. triethanolamine, may be added to assist this deaggregation and dispersion process.

The material may then be exposed to water or an aqueous solution, eg. dilute acid solution, to allow dissolution of the calcium as calcium hydroxide or a soluble calcium salt.

In the method according to the present invention the calcium dissolution step may be carried out with the assistance of heating and other suitable agents, eg. mechanical agitation or stirring.

After calcium has been dissolved over a sufficient period of time, the calcium ion-containing solution will generally have suspended therein particulate solid material whose content will depend on the composition of the original de-inking effluent or sludge and any treatment (eg. incineration) which has been applied to it. The solid particulate material may be separated from the calcium ion-containing solution by

one or more suitable known separation techniques, eg. filtration, evaporation or by use of a hydrocyclone or a centrifuge.

After the solid material has been separated the calcium ion-containing solution may be treated to form an insoluble calcium salt precipitate. An alkali metal salt, eg. a sodium salt, may be added to provide the required anion. For example, sodium carbonate may be added to the calcium ion-containing solution to produce a calcium carbonate precipitate.

Where the calcium ion-containing solution comprises calcium chloride sodium chloride is left in solution.

Alternatively, where the calcium ion-containing solution comprises a dissolved calcium salt, an alkali metal hydroxide, eg. sodium hydroxide, may be added to release calcium hydroxide.

Where the calcium ion-containing solution contains calcium hydroxide, formed either by dissolution of calcium oxide or by addition of an alkali metal hydroxide to a calcium salt solution, carbon dioxide may conveniently be added to the calcium hydroxide solution to form a calcium carbonate precipitate. Formation of precipitated calcium carbonate by addition of carbon dioxide to calcium hydroxide is, of course, well known.

The insoluble calcium salt product may be separated from the aqueous medium in which it is formed by a suitable separation process, eg. one of those specified hereinbefore. The product may be stored and thereafter supplied for use in one of the applications described hereinafter, especially as a particulate filler in the manufacture of paper. Where the solution contains little dissolved material after formation of the calcium salt precipitate, eg. after calcium hydroxide has been converted to calcium carbonate using carbon dioxide, the suspension or slurry containing the precipitate may itself be used optionally with partial dewatering.

For example, the suspension may be delivered to a paper mill for use of the suspension as a particulate filler supply for use in paper manufacture.

If the solution in which the insoluble calcium salt precipitate is produced contains dissolved species these may optionally be recovered and re-used. For example, where the dissolved species comprises sodium chloride solution this may be electrolysed in a known way to produce sodium hydroxide plus hydrogen and chlorine gases. The gases may be recombined to produce hydrogen chloride from which hydrochloric acid can be recovered which can be re-cycled for re-use in the acid dissolution step. The sodium hydroxide can be recycled for re-use as the alkali metal hydroxide for addition to the calcium ion-containing solution. In addition, carbon dioxide is produced in the dissolution step this may be re-cycled for re-use in the precipitation step. In this way, the need to purchase chemical reagents and to dispose of by-products can be minimised or avoided.

Where the dissolution of calcium is carried out on the effluent or sludge prior to any burning step, the particulate material separated from the calcium ion-containing solution may, preferably after drying, be heat treated to calcine the clay particles present.

The heat treatment may comprise incineration wherein organic and carbonaceous material contained in the solid material is removed by oxidation. The heat treatment may be carried out in a controlled manner as described in Applicant's GB9606638.6.

The calcined clay composition produced by calcination or incineration either before or after calcium dissolution may be employed as a pozzolanic material, eg. as a cement or concrete additive or for brickmaking.

Where it is the de-inking sludge itself which has been treated by acid dissolution causing calcium carbonate to be dissolved, the calcined clay composition will not suffer

substantially from the abrasiveness normally caused by incinerating kaolin and calcium carbonate together. In this case, the calcined clay composition may be used in other applications, eg. paper making.

The method according to the present invention beneficially allows minimisation of the amount of solid waste from a de-inking plant thereby reducing or eliminating the cost and environmental impact of disposal of such waste. Furthermore, the method allows a useful product, namely a precipitated insoluble calcium salt to be recovered.

Such product, for example calcium carbonate, may be recovered without the dark colouration normally associated with de-inking reject and is suitable for use in the various applications in which precipitated calcium salts, eg. calcium carbonate, are known to be useful, eg. as a particulate filler or extender material in paper, polymers, paints and the like or as a coating pigment or colour ingredient for coating of paper, paper board, plastic papers and the like.

Other particulate materials, eg. silicate and aluminosilicate material contained in the de-inking reject may, as described hereinbefore, be converted into useful products, eg. pozzolans, and the reagents used in the method according to the present invention may be recycled thereby minimising reagent costs and waste disposal.

Embodiments of the present invention will now be described by way of example with reference to the accompanying drawings in which:

Figures 1 to 4 are schematic flow diagrams of alternative methods embodying the invention.

As shown in Figure 1, in a first example of a method embodying the invention, input solid-containing material 1, preferably in the form of an aqueous suspension, comprises, reject sludge from a paper de-inking plant (not shown) or, alternatively, ash from an incinerator (not shown) which has

been employed to incinerate reject sludge from a paper de-inking plant.

The material 1 is subject to an acid dissolution step in a vessel 3 in which calcium present in the input material is dissolved as a soluble salt, eg. calcium chloride, by use of dilute hydrochloric acid. The suspension formed by the acid dissolution step is subject to a solid/liquid separation step in a separator 5. Solids obtained by the separation step in the separator 5 is either discarded as reject 7 or (where the input material has not been incinerated) is delivered to an incinerator 9, eg. operated at a temperature of 800°C to 1200°C as appropriate, which oxidises the organic material present in the solids and produces an inorganic product 11 comprising predominantly calcined kaolin (metakaolin) which may be used in pozzolan applications. The solution separated by the liquid/solid separation step in the separator 5 may be delivered to a vessel 11 in which sodium carbonate is added in a quantity calculated to give a required amount of precipitated calcium carbonate according to the amount of calcium present. The solution entering the vessel 11 may be monitored on-line by a monitor 13 to determine its calcium ion concentration and hence the required concentration of sodium carbonate in the vessel 11. The solution separated by the liquid/solid separation in the separator 5 may alternatively be delivered to a vessel 15 via a line also monitored by a monitor 13 in which sodium hydroxide solution is added to the solution to form calcium hydroxide which will dissolve in the water present up to its limiting solubility. Carbon dioxide is added in a reactor 17 (which may be the same as the vessel 15 or a separate reactor). The required amount of carbon dioxide to be added may, as an indication, be calculated from the amount of calcium hydroxide present which in turn can be determined from the concentration of calcium ions monitored by the monitor 13. It is not essential to calculate the required amount of carbon dioxide since after all calcium hydroxide has

been consumed the pH of the solution will drop indicating that the reaction has terminated.

The precipitate-containing slurry formed either in the vessel 11 or in the reactor 17 is subjected to dewatering, eg. by evaporation, in a concentrator 19. Output material 21 in slurry or dry powder form, as appropriate, from the concentrator 19 is delivered to a storage tank 23 for onward supply to a user plant, eg. a paper making mill or plant in which the material 21 is to be used as a paper filler material.

Liquid 22 separated by the concentrator 19 may be discharged as effluent or may be treated to recover reagents therefrom. For example, where the liquid 22 comprises predominantly sodium chloride solution, this may be electrolysed to produce hydrogen and chlorine and to leave sodium hydroxide. The hydrogen and chlorine may be combined to produce HCl for re-use in the acid dissolution step in the vessel 3 leaving, from the electrolysis, sodium hydroxide in the vessel 15 which may be re-used.

An alternative method embodying the present invention is illustrated in Figure 2. In this case, input material 25 comprises de-inking plant effluent sludge preferably diluted with clean water. This material 25 is delivered to an acid tolerant vessel 27 in which dilute hydrochloric acid is added. The suspension remaining in the vessel 27 is subjected to liquid/solid separation in a separator 29. The solid separated may be washed in a washer unit 31 and thereafter dried in a dryer 26 and incinerated in an incinerator 28. Heat energy 36 is generated by the combustion of organic material in the incinerator 28 and the solids output or ash from the incinerator indicated by output 34 comprises predominantly calcined clay (metakaolin) which may be employed as a pozzolanic material.

The solution indicated as 30 separated by the separator 29 and/or by the washer unit 31 is delivered to a concentrator 33. Extracted water 32 may be re-used in the washing unit 31. The solution concentrated by the concentrator 33 comprising mainly calcium chloride is delivered to an electrolytic cell 35. Hydrogen 37 and chlorine 39 are produced by the cell 35 and are delivered to a reactor 41 in which they are reacted to form hydrogen chloride gas 42. The HCl gas 42 may be recycled after dilution as dilute hydrochloric acid for addition in the vessel 27.

A calcium hydroxide-containing slurry formed by electrolysis of calcium chloride in the cell 35 is delivered to a reactor 43, in a metered amount, and an appropriate amount of carbon dioxide 45 which may be obtained as a by-product from the acid dissolution in the vessel 27 is supplied to the reactor 43 to provide conversion of the calcium hydroxide present to precipitated calcium carbonate. The product slurry formed may be concentrated by dewatering in a concentrator 46 and delivered to a storage tank 47 for onward delivery as a product, eg. as a particulate filler in paper manufacture. Alternatively, the product slurry formed in the reactor 43 may be delivered via the storage tank 47 for use without dewatering. Water 46 obtained from the dewatering process in the concentrator 46 may be recycled for dilution of the HCl output 42.

A further alternative method embodying the present invention is illustrated in Figure 3. In this case, input material 49 comprises ash from an incinerator (not shown) which has been employed to incinerate the solids content of reject sludge from a paper de-inking plant (not shown). The input material 49 is formed to a slurry with clean water 50 in a vessel 51 and is then treated in slurry form in a vessel 53 (which may be the same vessel as the vessel 53 or a different vessel) by grinding to break the solid material into finer particles such that the calcium oxide present is sufficiently

released. The slurry containing ground particles is then transferred to a separator 55 in which the solids present are separated from the liquid solution. Any large particles present may be returned to be further ground in the vessel 53. Remaining solid particulate material 57 may be employed as a pozzolanic material.

Liquid separated by the separator 55 comprising calcium hydroxide in solution is treated in a reactor 59 by addition of an appropriate amount of carbon dioxide 60. A product 61 comprising an aqueous suspension of precipitated calcium carbonate is formed and is delivered to a storage container 63 for onward supply to a user process, eg. for use as a filler in a paper making process. Optionally, the product 61 may be dewatered in a concentrator 65. Water 66 recovered from the suspension by the concentrator 65 may be re-cycled for use in the vessel 51.

A further alternative method embodying the present invention is illustrated in Figure 4. In this case, as in Figure 3, input material, indicated by reference numeral 67 in Figure 4, comprises ash from an incinerator (not shown) which has been employed to incinerate the solids content of reject sludge from a paper de-inking plant (not shown). The input material 67 is formed with clean water 68 into a slurry in a vessel 69 and is then subjected to grinding in a vessel 71 to release calcium oxide particles which form a saturated calcium hydroxide solution in the slurry.

The slurry 70 formed in this way is then passed in turn through each of a series of liquid/solid separators 73a to 73e, eg. hydrocyclones, clean water being added to the treated slurry before passing through each separator.

The solid material recovered from the separators 73a to 73e may be rejected or used as a pozzolanic material 74. Any large particles present may be returned to the vessel 71 for further grinding. The liquid produced following separation in the separators 73a to 73e comprises calcium hydroxide solution

76 which is delivered to a reactor 75 where it is treated by addition of an appropriate amount of carbon dioxide 78. A product 77 comprising an aqueous suspension of precipitated calcium carbonate is formed and is delivered to a storage container 79 for onward supply to a user process, eg. for use as a filler in a paper making process.

Optionally, the product 77 may be dewatered in a concentrator 81. Water 80 recovered from the suspension by the concentrator 81 may be re-cycled for use in the vessel 69 or in the slurry delivered between the separators 73a to 73e.

The purpose of having multiple separators in the method illustrated in Figure 4 is as follows. The solubility of calcium hydroxide is low although much higher than calcium carbonate. A considerable amount of calcium hydroxide remains undissolved at each separator and is removed with solids. Hence, when the solids pass from one separator to the next fresh water must be added to obtain further dissolution. In practice, the cycle is continued through a sequence of separators until all of the calcium hydroxide has dissolved.

CLAIMS

1. A method of treating solid containing material derived from effluent or sludge from a plant for de-inking paper, the material containing calcium in the form of one or more insoluble calcium compounds, the method including the steps of treating the material to cause dissolution of the calcium thereby forming a calcium ion-containing solution in which insoluble solids are suspended, separating the solution from the insoluble solids and adding to the solution one or more reagents to form a calcium salt precipitate.

2. A method as in claim 1 and where the treated solid containing material comprises the said effluent or sludge, optionally after diluting with water, the said calcium compound comprises calcium carbonate and/or sulphate.

3. A method as in claim 1 and wherein the treated solid material comprises ash obtained by incinerating the solid content of the de-inking effluent or sludge and the material includes calcium oxide and optionally one or more other calcium compounds.

4. A method as in claim 1, 2 or 3 and wherein the treatment to cause dissolution includes adding a dilute acid.

5. A method as in claim 4 and wherein as added reagents sodium hydroxide is added to the solution separated by the separation step to form calcium hydroxide and then carbon dioxide is added to the calcium hydroxide formed to form a calcium carbonate precipitate.

6. A method as in claim 4 and wherein as added reagent sodium carbonate is added to the solution separated by the separation step to form a calcium carbonate precipitate.

7. A method as in claim 3 and wherein the treated solid material is comminuted prior to the dissolution step.

8. A method as in claim 4 or claim 7 and wherein the treated material in the dissolution step is dissolved in water to form calcium hydroxide solution to which carbon dioxide is subsequently added in the precipitation step to form a calcium carbonate precipitate.

9. A method as in any one of the preceding steps and wherein the separation step is carried out using a series of liquid/solid separators in sequence.

10. A method as in any one of the preceding claims and wherein the calcium salt precipitate is separated from the aqueous medium in which it is formed.

11. A method as in claim 10 and wherein useful chemical species in the aqueous medium are recycled for re-use.

12. A method as in any one of the preceding claims and wherein the calcium salt precipitate is supplied for use as a particulate filler or pigment material.

13. A method as in claim 1 and substantially as hereinbefore described with reference to any one of Figures 1 to 4 of the accompanying drawings.

The Patent Office

15

Application N : GB 9616037.9
Claims searched: 1 - 13

Examiner: Michael R. Wendt
Date of search: 21 October 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): CIC (CACD, CACF, CRAL, CRCF, CJB, CKB, CM)

Int Cl (Ed.6): C02F 1/52, 1/58, 9/00, 11/00, 11/14

Other: WPI, Claims, Japio, CAS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	NOTHING RELEVANT FOUND	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.